Stereochemistry of the Photochemical Berson-Willcott Rearrangement of Methyl 2,3-Benzonorcaradien-7-ylacetate to Methyl 2,3-Benzobicyclo-[3.2.0]hepta-2,6-dien-4-ylacetate

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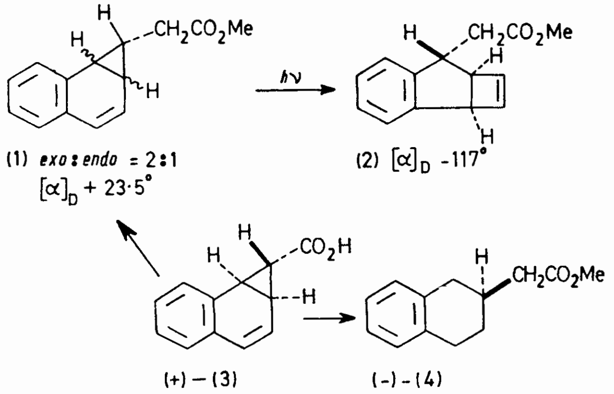
Summary The photochemical Berson-Willcott skeletal rearrangement of methyl 2,3-benzonorcaradien-7-ylacetate to methyl *anti*-2,3-benzobicyclo[3.2.0]hepta-2,6-dien-4-ylacetate was found to proceed with inversion of configuration at C-7.

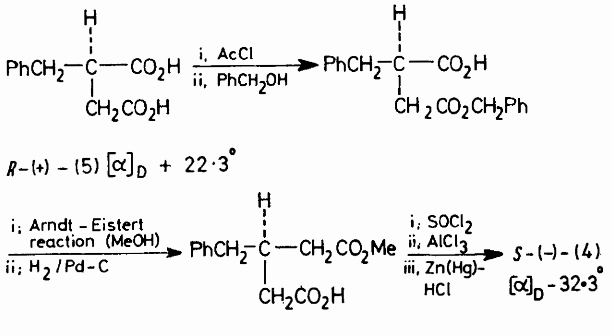
In a previous paper,[1] we described the photochemical rearrangement[2] of methyl 2,3-benzonorcaradien-7-ylacetate (**1**) to give a series of compounds, including methyl *anti*-2,3 benzobicyclo[3.2.0]hepta-2,6-dien-4-ylacetate (**2**)† which was obtained in a highly stereospecific manner.



Scheme 1

To clarify the stereochemical course of the photochemical rearrangement of (**1**) to (**2**)‡ the absolute configurations of the starting material (+)-(**3**) and the resulting product (—)-(**2**) had first to be established because it is known that the acid (**3**) is fixed rigidly as the *exo*-structure but (**1**) is susceptible to the thermal and photochemical Cope rearrangement to an *exo-endo* mixture with retention of the configuration at C-7.[1,3]

Catalytic hydrogenation of (+)-(**3**), $[\alpha]_D$ +150°, followed by treatment with CH_2N_2, gave a hydrogenolysis product (**4**) along with a dihydroester. The *S*-(—)-configuration of (**4**) was confirmed by correlating it with *R*-(+)-benzylsuccinic acid (**5**)[4] (Scheme 2). The configuration at C-7 of (+)-(**3**) was thus determined as *R*.



Scheme 2

In order to determine the absolute configuration of (—)-(**2**), diethyl 1,2-benzocyclohepta-1,3,5-trien-7-ylmalonate[5] was hydrolysed to the diacid, whose optical resolution was carried out through its brucine salt to give the (+)-diacid

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† Previously, we could not identify the *syn*-isomer of (**2**), but careful examination of the photolysis products by v.p.c. and n.m.r. spectroscopy allowed us to estimate its formation along with (**2**) in the ratio of 5 : 95.

‡ The optical rotations of the compounds described in this paper were measured in 95% EtOH solutions. All compounds showed satisfactory analytical data.

(**6**), $[\alpha]_D$ +202°. The diacid was decarboxylated to the mono acid, which was converted to its methyl ester (**7**), $[\alpha]_D$ +78°. The (+)-ester (**7**) underwent a photochemical disrotatory ring closure to (+)-*anti*-(**2**), $[\alpha]_D$ +145°. On the other hand, (+)-(**7**), $[\alpha]_D$ +78°, was hydrogenated to a (−)-tetrahdro derivative (**8**), $[\alpha]_D$ −23°. The absolute configuration of (+)-(**8**) was established to be *S* by correlating it with *R*-(+)-(**9**) (Scheme 3). Homologation of the optically impure (+)-acid (**9**),[4] $[\alpha]_D$ +16·7°, to the methyl ester (**10**), $[\alpha]_D$ +14·7°, was achieved using Arndt-Eistert conditions. Ring enlargement of (+)-(**10**) using diazomethane–BF_3 in ether[6] gave a mixture of ketones, which were reduced to methylene esters using the tosylhydrazine and sodium cyanoborohydride technique in sulpholane–DMF.[7] G.l.c. separation of the methylene esters gave *S*-(+)-(**8**), $[\alpha]_D$ +9·6°, which was identical with the sample obtained by hydrogenation of (+)-(**7**), but of opposite optical rotation.

Thus the photochemical rearrangement of (**1**) to (**2**) proceeded with inversion of the configuration at C-7 of the norcaradiene system through (**7**), possibly *via* a transient intermediate like (**11**), in agreement with orbital symmetry considerations.

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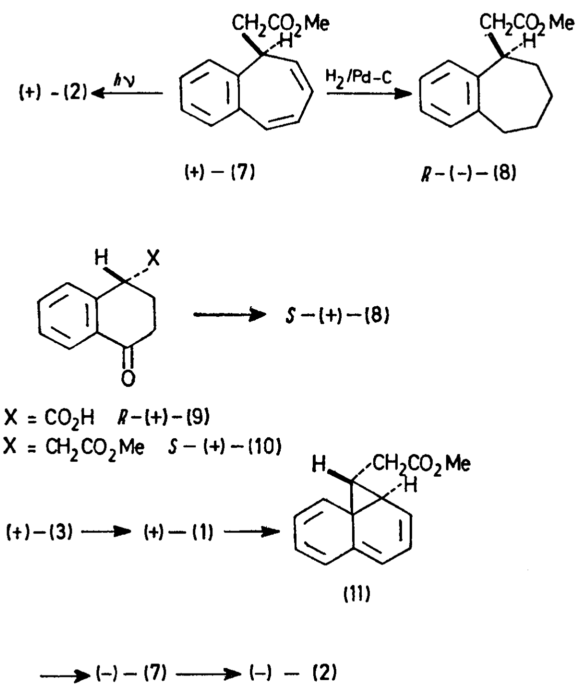

Scheme 3

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